

Oxygen and Carbon Impurities and Related Defects in Silicon

Charles W. Pearce
AT&T Technology Systems
Allentown, Pa.

Oxygen and carbon are the predominant impurities in Czochralski-grown silicon. Their concentrations usually exceeding those of any intentional dopants. The behavior of these impurities during the heat treatments characteristic of device processing generally determines the defect morphology of the processed wafer. As a result this topic has been considerably researched. This paper will review the topic starting with the incorporation of oxygen and carbon during crystal growth and proceed to a discussion of device effects.

Specifically, methods for controlling oxygen and carbon incorporation during crystal growth will be discussed and results supporting a segregation coefficient of $k=0.5$ for oxygen will be presented. The nucleation and precipitation behavior of oxygen is complex. This paper will focus on temperature and doping level effects which add insight into the role of point defects in the nucleation process. In general precipitation is found to be retarded in N^+ and P^+ silicon. The types and quantities of defects resulting from the oxygen precipitates is of interest as they are technologically useful in the process called "intrinsic gettering". A comparison will be made between the available defect sites and the quantities of metallic impurities present in a typical wafer which need to be "gettered". Finally, a discussion of the denuded-zone, intrinsic-gettered (DZ-IG) structure on device properties will be presented.

Introduction

Oxygen and carbon are important impurities in Czochralski-grown silicon as the defect morphology of a processed wafer often depends on the behavior of these impurities during the heat treatments used in device fabrication. In particular, denuded zone (DZ), intrinsic gettering (IG) techniques (1) are used to improve the yield and performance of bipolar and MOS devices. These DZ-IG techniques transform oxygen into a beneficial impurity. Because of this technological importance the subject of oxygen in silicon has been considerably researched and periodically reviewed (1, 2, 3). The present state of the art includes the following observations. Oxygen is now considered a controllable impurity in Czochralski (CZ) silicon. Most supplies of silicon wafers will supply material to a specification. Secondly, there is an assort-

ment of published heat treatments which can be used on wafers to develop a "denuded zone", i.e., a near surface region free of oxygen-related defects, and an interior "intrinsically gettered zone" where the precipitation of oxygen and related defects is promoted. These treatments involve heat treatments at different temperatures to outdiffuse oxygen for a denuded zone, nucleate and precipitate oxygen, and promote the growth of defects resulting from the precipitation process. Figure 1 illustrates a typical cycle. Although such methods allow for the control of oxygen during processing, questions still remain as to the fundamental aspects of nucleation and precipitation. This is evident in the behavior of crystals grown to the same apparent oxygen content, but exhibiting markedly different precipitation behavior during device processes. To use a practical example we have observed situations where given the same level of oxygen content wafers from one supplier will readily precipitate during processing, whereas another vendor's material remains precipitate-free. Such observations have led to an interest in the role of point defects (i.e., vacancies and interstitials) in the nucleation process. Differences in precipitation behavior are thought to be related to the effect of the thermal cycles, a crystal receives in-situ in the grower, on the point defect populations (4). The role of carbon as a precipitation promoter is also being studied (5).

Another recent area of interest is the behavior of oxygen in N⁺ and P⁺ silicon. The use of N/N⁺ and P/P⁺ epitaxial silicon wafers for NMOS and CMOS devices (6, 7) has stimulated research into this area. Beyond the immediate technological importance studies of N⁺ and P⁺ silicon provide another avenue to evaluate the role of point defects in the nucleation process.

This paper will review the topic starting with oxygen incorporation and proceed to device effects with an emphasis on newer results.

Oxygen Incorporation

The quantity of oxygen incorporated into a growing crystal is at any point in time a function of the segregation coefficient and the oxygen content in the molten silicon (melt). The melt concentration depends on the erosion rate of the quartz crucible and the evaporation of SiO from the melt-ambient interface (8). Although the erosion rate is temperature dependent it is significantly increased by the presence of convection currents in the melt. In large crucibles characteristic of industrial-scale growers thermal convection effects are usually larger than those from forced convection. Given the Grashof number as an index of thermal convection (9). The melt turbulence tends to be reduced as the level of the melt decreases in the crucible during growth. Also, the surface area which is eroding simultaneously decreases. The net result is a decrease in the oxygen content of the melt. However, methods to alter the erosion rate or otherwise control the melt oxygen content have been found. These include the use of magnetic fields to suppress convection currents in the melt (10), double crucible techniques (11) which provide a constant erosion rate and surface area of an inner crucible, and reduced ambient pressure growth (12). In short, techniques exist which improve the uniformity of oxygen in an as-grown CZ crystal by 10X compared to unrefined CZ growth processes.

Beyond melt dynamics the influence of impurities on crucible erosion needs to be considered. The carbon reduction of SiO_2 into CO and SiO has already been shown to be a favorable reaction (8). Thus, higher levels of carbon in the melt increase the erosion rate. Note that since carbon has a low segregation coefficient ($k=.07$) it tends to enrich in the melt as growth proceeds thus increasing the crucible erosion rate. We have noticed a similar effect for boron. As seen in Table I crystals grown with high levels of boron tend to exhibit a higher oxygen content when grown under otherwise identical conditions. This is attributed to the glass forming properties of boron because similar melt levels of antimony a non-glass former do not increase the level of oxygen. This fact needs to be considered when comparing the behavior of P-, P+ and N+ crystals. It cannot be tacitly assumed identical growth conditions result in identical oxygen levels.

Fundamental to understanding dopant incorporation is an accurate value for the segregation coefficient. For many years the value for oxygen was generally accepted as $k=1.25$. Such a value was extracted from the axial distribution of oxygen in an as-grown crystal. However, in hindsight the substantial variation in melt oxygen content due to the convection effects just discussed render such an approach invalid. Recent experimental work by Lin (13) suggests a value of $k=0.25$. We have calculated k from first principles and re-evaluated existing solubility data for the liquid and solid phases and similarly conclude $k=0.5 \pm .25$ (14).

A related issue to the incorporation of oxygen is the method by which it is measured. The most common method is infrared (IR) absorption measurements at 1106 cm^{-1} . However, the measurement is sensitive only to oxygen in interstitial lattice sites and needs to be calibrated with another analytical method. In fact, five calibration constants have been reported (15, 16, 17, 18, 19). Secondary Ion Mass Spectrometry (SIMS) and Charged Particle Activation Analysis (CPAA) have also been used for oxygen determinations. In our experience the CPAA does seem to indicate more oxygen than the IR method by about 50% (Table I). However, due to uncertainties in the calibration of each technique and the oxygen inhomogeneity within a sample it is unclear whether a real difference is present. Evidence of a real difference comes from Jastrzebski (20) who has heated wafers at high temperatures (1200-1300°C) and observed increases in the IR oxygen content of up to 2X. This indicates a substantial amount of oxygen in non-interstitial sites in the as-grown crystal. However, we have not observed a similar increase upon heating in our crystals. This leaves open the question of whether precipitation differences in material are due to nucleation effects or simply a difference in oxygen content. If the latter is true it means any calibration constant for IR measurements is good only for the material on which it was produced.

Nucleation and Precipitation

The particulars of the nucleation process have been a source of controversy for some time. Discussions have centered on whether the nucleation is homogeneous or heterogeneous and if heterogeneous the nature of the nuclei. Specifically, the role of interstitials and vacancies.

Insight into these questions can be gained from a study of N+ and P+ silicon.

We have observed (6) as has De Kock and van de Wijgert (7) that precipitation is suppressed in N+ silicon above a doping level 1×10^{18} atoms/cm³ when heated at high temperatures ($T=1000^\circ\text{C}$). However, given a suitable heat treatment (24 hr-700°C, 24 hr-900°C, ref. 19, 6) precipitates can be formed. At still higher N+ doping levels (5×10^{19} atoms/cm³) no precipitates are observed even given the heat treatment just described. Furthermore, the lack of precipitation in N+ silicon is not due to a lower oxygen content as discussed in the prior section. Additionally, we have found that precipitation is retarded, but not totally suppressed, at doping levels of 5×10^{19} atoms/cm³ for boron-doped silicon. Doping levels of 9×10^{19} atoms/cm³ still exhibit precipitation, but at densities up to 10^2 less than densities in P- samples given the same heat treatment (Figure 2). These results are consistent within a framework of a vacancy model. Vacancies in silicon exist in three charge states and a neutral configuration (21). The levels are shown in Figure 3. For n-silicon a movement of the Fermi level towards the conduction band means negatively charged vacancies become the dominant point defect. If these negative vacancies pair with oppositely-charged dopant atoms then they are unavailable for nucleation as proposed by De Kock (7). In p silicon a similar movement of the Fermi level will not produce a dominance of positively-charged vacancies as the energy level for the V+ lies much closer to the valence band edge. So even at high p doping levels some neutral vacancies still exist so some precipitation does occur. The available data does not conclusively prove the role of vacancies, but does indicate the role of point defects having asymmetric energy levels within the band gap.

Device Issues

DZ IG treatments produce bulk stacking fault (BSF) densities in the 10^9 - 10^{10} BSF/cm³ range. Typical metallic impurity contents of processed wafers are in the 10^{12} - 10^{15} atoms/cm³ (22). At either extreme complete capture (gettering) of impurities by defects requires 10^2 - 10^4 atoms/BSF. Given a typical BSF circumference of 10 microns a fault need only capture 10^{-4} - 10^{-2} atoms/Å. Thus, the fault need only retain a relatively few atoms along its perimeter. This does not appear to be the limiting feature of intrinsic gettering. The limitations of IG probably stem from other sources. First, although BSF do exhibit a net capture of impurities it is not known how efficient this process is compared to other capture processes such as ion pairing in phosphorous gettering. Secondly, the capture of a metallic impurity at a BSF does not neutralize it electrically. Rather removal of a metallic impurity from the depletion region of a device to a BSF in the interior of the wafer results in the impurity being changed from a factor in diffusion rather than generation current. As such a net improvement in junction leakage will result, but the leakage current will now be a function of DZ width. Increasing the DZ width can only be accomplished up to half the thickness of the wafer at the expense of the number of gettering sites. The IG region remains a region of high recombination for photoexcited carriers.

Conclusion

In spite of considerable research into this topic full and final answers to some questions are still not obtainable, but there exists a sufficient body of data and information to successfully control the behavior of oxygen in CZ silicon. In particular, the study of heavily-doped silicon offers new insights into nucleation and precipitation processes.

Comparison of Oxygen Contents of Silicon as a Function of Doping Level and Type

Table I

	<u>IR</u>	<u>CPAA</u>
n+ (.02 ohm-cm.)	-	1.5×10^{18}
n+ (.02 ohm-cm.)	-	1.9×10^{18}
p- (5 ohm-cm.)	1.1×10^{18}	1.5×10^{18}
p- (5 ohm-cm.)	0.8×10^{18}	2.1×10^{18}
p- (5 ohm-cm.)	1.0×10^{18}	1.1×10^{18}
p- (.01 ohm-cm.)	-	1.3×10^{18}
p++ (.001 ohm-cm.)	-	2.7×10^{18}
p++ (.001 ohm-cm.)	-	2.5×10^{18}

References

1. C. W. Pearce, L. E. Katz and T. E. Seidel, "Semiconductor Silicon 1981", edited by H. R. Huff and R. J. Kriegler, The Electrochemical Society, Pennington, N.J., p. 705.
2. J. R. Patel, *ibid*, p. 189.
3. W. M. Bullis and L. C. Kimmerling eds., "Defects in Silicon", The Electrochemical Society, Pennington, N.J., 1983.
4. H. Nakanishi, *Jpn. J. Appl. Phys.*, 19, 561 (1980).
5. J. Leroueil, *Phys. Stat. Sol. (a)* 67, 177 (1981).
6. A. J. R. De Kock and W. M. van de Wijgert, *J. Crystal Growth*, 49, 718 (1980).
7. C. W. Pearce and G. A. Rozgonyi, "VLSI Science and Technology - 1982", edited by C. J. Dell'Oca and W. M. Bullis, The Electrochemical Society, Pennington, N.J., p. 53.
8. S. M. Sze, editor, "VLSI Technology", McGraw Hill, N.Y., 1983, p. 26.
9. J. R. Carruthers et al, "Semiconductor Silicon 1977", H. R. Huff and E. Sirtl eds., The Electrochemical Society, Pennington, N.J., p. 61.
10. T. Suzuki et al, "Semiconductor Silicon 1981", H. R. Huff and R. J. Kriegler eds., The Electrochemical Society, Pennington, N.J., 1981, p. 90.
11. W. Lin and C. W. Pearce, *J. Appl. Phys.*, 51 (10), 5540 (1980).
12. W. Lin and D. W. Hill, "Silicon Processing", D. C. Gupta ed., The American Society for Testing and Materials, Phila., Pa., 1983, p. 24.
13. W. Lin and D. W. Hill, *J. Appl. Phys.*, 54, 1085 (1983).
14. C. W. Pearce and R. J. Jaccodine, "Defects in Silicon", W. M. Bullis and L. C. Kimmerling eds., The Electrochemical Society, Pennington, N.J., 1983, p. 115.
15. Y. Yatsurugi et al, *J. Electrochem. Soc.*, 120, 975 (1973).
16. W. Kaiser and P. H. Keck, *J. Appl. Phys.*, 28, 822 (1957).
17. K. Graff et al, *Sol. State Elec.*, 16 887 (1973).
18. J. A. Baker, *ibid*, 16, 1431 (1970).

19. T. Sizuka et al, "Defects in Silicon", W. M. Bullis and L. C. Kimmerling eds., The Electrochemical Society, Pennington, N.J., 1983, p. 265.
20. L. Jastrzebski et al, J. Electrochemical Soc., 124 1638 (1982).
21. J. A. Van Vechten and C. D. Thurmond, Phy. Rev. B, 14, 3551 (1976).
22. P. F. Schmidt and C. W. Pearce, J. Electrochem. Soc., 128, 630 (1981).

ORIGINAL PAPER
OF POOR QUALITY

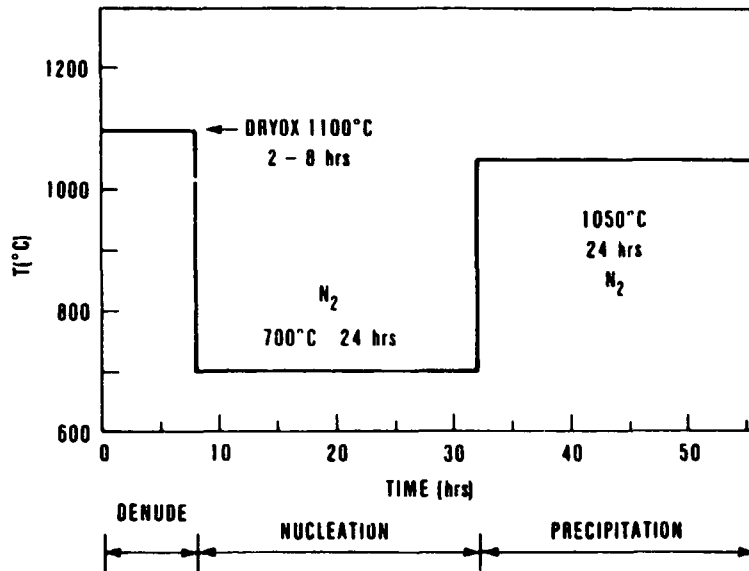


Figure 1. Hi-Lo-Hi Thermal Cycle for Intrinsic Gettering

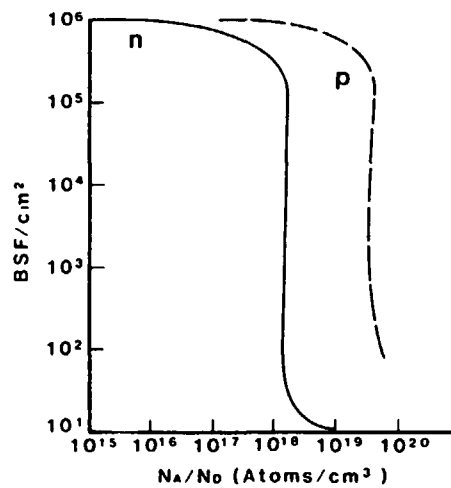


Figure 2. Doping Density Effect on Defect Density

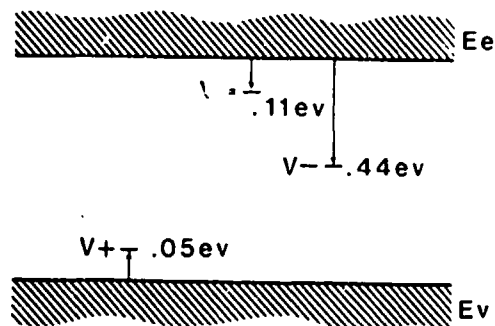


Figure 3. Estimated Vacancy Energy Levels in Silicon

DISCUSSION

SAH: The denuded zone gettering -- can you have a heavily doped region there that also could be used as the region for intrinsic gettering, like the region you are talking about where eventually you have a large concentration of metallic impurities?

PEARCE: Are you asking if you can have a denuded zone in something very heavily doped?

SAH: Yes. Denuded zone in front of a very heavily doped region; that heavily doped region is the region that would getter.

PEARCE: The structure that I mentioned earlier, the pp^+ . One of the reasons that it works so well is that we form a denuded zone in the p^+ substrate, and then the heavy doping plus the precipitation there captures all the impurities. That turns out to be a very efficient structure for impurity capture. The heavy doping then reduces minority carrier concentrations so there are very few electrons available using the doping level for diffusion current. This is why we get these fantastic lifetimes.

LESK: Could you not measure the distribution coefficient of oxygen in silicon directly by using one of the melt refreeze techniques, where within a matter of five or 10 seconds you have melted and refrozen, and just look at the difference in oxygen content on either side of the interface?

PEARCE: Yes. I guess you could. We were looking for a fast answer and did some of the things we had done and when elected to do the variation of pull rate -- it's just amazing that we had the wrong number for so many years.

SWANSON: Some one, years ago -- I think it was Rohatgi -- reported that he was able to lower the oxygen concentration with HCl oxidations below the solid solubility at 1250°C where the oxidations were being done. We took some Cz wafers, 100 micrometers thick, and repeated his treatment, which according to the report would have depleted the oxygen almost completely from the wafer, and also gave a float-zone wafer the same treatment. The float-zone wafer had a high lifetime after this and the Cz wafer did not. Do you have any feeling maybe why that would be the case, or what we did wrong?

PEARCE: The work with the HCl -- I was involved in that with George Rozgonyi -- and we had done some stuff each way. We did it with and without HCl and at that time it looked like the HCl did give a pronounced improvement. We even had some charged-particle data that seemed to support that. I think, in retrospect, we were just seeing some samples of sample fluctuation. Maybe the role of the HCl wasn't as large as we had originally expected. There is a recent paper out of Penn State, and some others, which shows that in the presence of chlorine, at high temperatures, the diffusivity of oxygen is increased, and they have an interstitial vacancy model, so I guess it does have an effect. I guess it is an effect mostly on the diffusivity rather than on anything else.

SWANSON: Then you really see no strong evidence that the oxygen concentration is below solid solubility at the processing temperature?

PEARCE: It is probably not below the solid solubility.

RAI-CHOUDHURY: There is some evidence that this oxygen precipitates, although these precipitates behave as recombination sites or generation sites. Especially if you put in diodes, looking at the diode characteristics. Do you have any data to show what kind of electrical activity these precipitates have? Can you comment on that?

PEARCE: We don't have any direct evidence on the precipitates. There was some early EBIC work by Kimmerling at Murray Hill that showed decoration or impurities around the circumference of the fault, so that has been more or less proved. There was also some work by -- I think it was Varker, out of Motorola -- doing some diode measurements on things that were precipitated with no extended defects and it did show a degradation in lifetime. I personally have not done anything, but there are some data that support that the precipitates apparently attract metallic impurities as well as gettering centers and show the same effect.

LANDSBERG: Do you have any views about the incorporation of defects as you lower the temperature? After you have had a high solubility at a higher temperature, some of these oxygen -- or defects of some kind -- will get incorporated? I am looking for people who know how to describe this or whether there are some rules or some laws on that.

PEARCE: One of the things we felt, at least with metallic impurities, is that -- we call them saucer pits, fog, haze, things like this -- you go through an oxidation, do an etch, you find a small density of pits. One of the things we have found is that metallic impurities will precipitate very rapidly, so that if you cool the material fairly slowly, starting at some high temperature down to some low temperature, you can precipitate the metallics, or so-called saucer pits. But now, since they are not in solution, the lifetime tends to go up in many cases. On the other hand, if you quench the material -- very rapid cooling keeps all the metallics in solution -- the lifetime is low. So a lot of the effects people see with leakage currents and lifetime in silicon deal with how they cool the material out of the furnace, and the particulars of the metallics that they have present. But even very small changes in pull rate will dramatically affect the amount of precipitates that form.

LANDSBERG: Right. Are there any sort of systematic studies with this?

PEARCE: There is some good work in some of the semiconductor silicon series, like 1981 Electrochem Society, on defects in silicon -- out of the San Francisco meeting, I guess, last year. Yes, there are some papers I can give you the references on.

LANDSBERG: But there is no single law that kind of transpires as a result of all this, like in my talk I used -- a number of times -- E to some energy divided by some temperature?

PEARCE: Well, there is some work by Graff and co-workers who look at how these things precipitate as a function of solubility and diffusivities. You can start with that kind of information and see how something like a titanium would precipitate relative to an iron, and he has been able to predict that some of the metallics will be haze formers, etc. That is pretty good work. That is published in a 1981 volume.

CHENG: I just heard you mention that the wafer can be denuded up to 100 micrometers. This seems to ring a bell for solar-cell people, since people can make a four-mil cell thickness. Could you say some more how that is processed?

PEARCE: Yes. It basically is a time-temperature thing. We did a lot of denuding up at 1250°C, and at that temperature, if you go for something 20 hours, or whatever, one can denude into some very high thicknesses. On this graph here, Curve No. 1, is the work we did at 1250°C and at several hundreds of minutes you can get up over 100 micrometers denuding. There is a book out, VLSI Technology, edited by S.M. Sze, and the first chapter has the experimental data at 1250°C versus time.

SAH: I have just one more question: p-p process gave very good results, so how about nn⁺ or pn⁺ or np⁺? Is there any indication that you would expect the same or different results?

PEARCE: The problem with n on n⁺ is that it doesn't precipitate, of course, and we had a paper that we published, "VLSI," it was in the Electrochem Detroit meeting, the first VLSI Symposium, in 1982. The problem with n on n⁺ is that there are no intrinsic getter sites, so all the impurities tend to go to the surface and you get a lot of precipitates at the surface, and it is very poor material. To get the so-called intrinsic gettering to work in nn⁺ you have to go up to something above 5×10^{19} . There has been some work published on phosphorus gettering as to what concentration level you need. It is around 5×10^{19} , so you have to get a substrate level up to there. There was some work at RCA where they did that. They grew some layers on some n⁺⁺ material and the lifetimes were quite high. It is just difficult to routinely grow epitaxial layers and grow background doping at those high levels of arsenic or phosphorus. Furthermore, the crystal growers don't like to grow crystals like that because of the hazards. But, yes, it does work if you get up to that level.

SIRTIL: You mentioned this distribution coefficient of oxygen. I would have some mixed feelings if you would call it theoretical distribution coefficient. If it is the effective distribution coefficient for Czochralski pulling, that would certainly be all right.

PEARCE: I would agree with that.

SIRTIL: The work of a Japanese scientist was an outstanding contribution to this particular point. What exactly he did was, he avoided escape of oxygen during zoning so that he got the ideal conditions in terms of oxygen incorporation. And if you'll just remember the diagram I showed during my talk in this case, ingot solidification in a mold is a nearly

ideal condition in this respect. You may have seen that we indeed have found a distribution coefficient higher than 1, and that was not just once. so I think that from the ideal standpoint, the Japanese work is really the true theoretical value.

PEARCE: Yes. I think one of the things that make people accept that is that if you take the slope of that one plot that we presented with the unrefined Czochralski growth, seed versus tail, and then use classic solidification theory to extract a k from that, you usually do get something greater than one. So that tended to reinforce that, even though what is called the effective value in Czochralski is probably something lower and was clouded by all the variation of oxygen within the melt. So I would agree with your comments.